

STUDIES OF ORGANOMETALLIC COMPOUNDS XXXVI. SYNTHESIS OF [1,2-BIS(ETHOXYCARBONYL)ETHYL]TIN TRICHLORIDE

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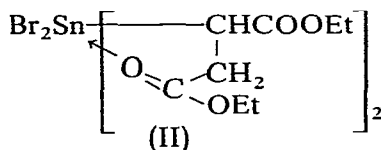
SUMMARY

[1,2-Bis(ethoxycarbonyl)ethyl]tin trichloride (III) was synthesized by the reaction of bis[1,2-bis(ethoxycarbonyl)ethyl]tin dibromide and stannic chloride.

Evidence is presented which indicates that (III) must be a five-coordinated structure containing a five-membered ring structure and there must also be intermolecular interaction between tin and the β -carbonyl group in the solid state.

INTRODUCTION

Bis[1,2-bis(ethoxycarbonyl)ethyl]tin dibromide (II) has been obtained from



the reaction between tin foil and diethyl bromosuccinate (I)¹. It was considered that (II) had two stereoisomers^{1,5,6} with six-coordinated Sn containing the five-membered ring structure¹⁻⁸ shown. X-ray diffraction studies^{5,6} of these stereoisomers confirmed this ring structure.

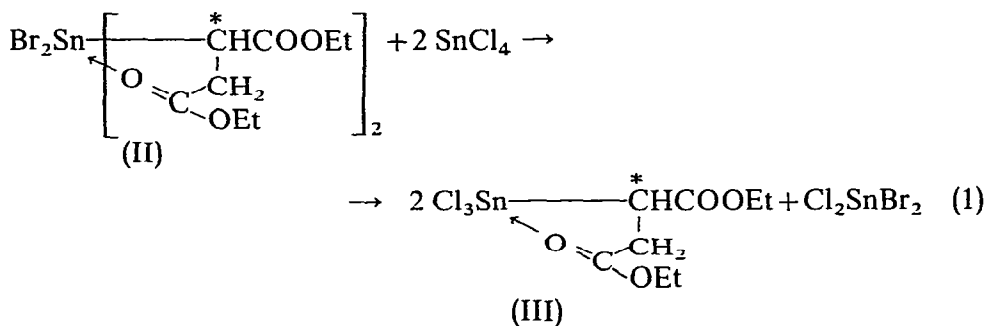
In this study, the organotin trichloride (III) was synthesized from (II) by reaction with stannic chloride. The molecular structure of the product is of interest since intramolecular coordination and intermolecular interaction of C=O groups to tin seem to occur.

DISCUSSION

The crystalline product which was obtained from the reaction of (II) with an excess of stannic chloride, was formulated as [1,2-bis(ethoxycarbonyl)ethyl]tin trichloride (III) on the basis of elementary analyses and molecular weight data [eqn. (1)].

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Strong absorptions in the IR spectrum of (III) were observed at 1634 and 1692 (broad) cm^{-1} in the solid state and at 1718 and 1651 cm^{-1} in benzene solution. Those at 1634 or 1651 cm^{-1} , due to a markedly shifted carbonyl stretching vibration, indicate coordination of the γ -C=O group to tin. The other absorptions at 1692 and 1718 cm^{-1} were assigned to the C=O stretch of the ester group at the β -position. The broad absorption at 1692 cm^{-1} may be due to a shift of the carbonyl stretching vibration, which would be expected if there was an interaction between this C=O and another tin atom in solid state. Such intermolecular interaction seems reasonable since the tin atom is more electropositive in (III) than in (II).

NMR spectra of (I), (II) and (III) are investigated. The shielding values and coupling constants are shown in Table 1.

TABLE 1
CHEMICAL SHIFTS AND COUPLING CONSTANTS OF (I), (II) AND (III)

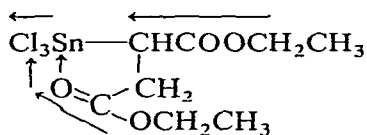
Compound	τ -values ($\Delta\delta^a$) (ppm)				J -values (Hz)		
	H ^a	H ^b	H ^c	H ^d	$J(\text{H}^a-\text{H}^c)$	$J(\text{H}^b-\text{H}^d)$	
$\text{BrCHCOOCH}_2\text{CH}_3$ $\quad $ $\text{CH}_2\text{COOCH}_2\text{CH}_3$ (I)	5.80	5.88	8.72	8.75	7.0	7.0	
$\text{Br}_2\text{Sn} \left[\begin{array}{c} \text{CHCOOCH}_2\text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{O}=\text{C}-\text{OCH}_2\text{CH}_3 \end{array} \right]_2$	(II) ^b	5.89	5.76	8.69	8.67	7.2	7.0
	(II) ^c	(+0.09)	(-0.12)	(-0.03)	(-0.08)	7.1	7.0
		(+0.05)	(-0.16)	(-0.02)	(-0.09)		
$\text{Cl}_3\text{Sn} \left[\begin{array}{c} \text{CHCOOCH}_2\text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{O}=\text{C}-\text{OCH}_2\text{CH}_3 \end{array} \right]$ (III)	5.65	5.52	8.66	8.56	7.0	7.5	
	(-0.15)	(-0.36)	(-0.08)	(-0.17)			

^a $\Delta\delta$ (figures in parentheses) is the difference of chemical shifts between (I) and the analogous protons (II) or (III). ^b Low-melting isomer (m.p. 114–115°). ^c High-melting isomer (m.p. 122–123°).

The chemical shifts of the ethoxymethylene proton bonded to the C=O at the β - and γ -positions with respect to the methine proton of (I) occurred at τ 5.80 ($J = 7.0$ Hz) and τ 5.88 ($J = 7.0$ Hz), respectively, but those for (II) at corresponding positions were τ 5.85–5.89 and τ 5.72–5.76, respectively. The relatively low field shift, as against that of the starting material (I), of the ethoxymethylene proton bonded to the C=O

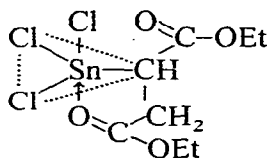
at the γ -position with respect to the methine proton (or tin atom) of (II) indicated that the C=O in the ester group at the γ -position with respect to the tin atom was coordinated to the tin atom, as already confirmed by the IR spectra and X-ray diffraction studies^{5,6}.

The ethoxymethylene and -methyl protons of (III), compared with those of (II), show relatively low field shifts. These shifts must also be a result of the shielding constant decreasing in proportion to the decrease in the electrons in these protons to the tin atom by three electronegative halogen atoms.



The large low field shift, as against that of (I), of the ethoxymethylene proton bonded to the C=O at the γ -position with respect to the tin atom, also indicated C=O coordination to the tin atom, as already suggested by IR spectrum.

Therefore, (III) was assumed to have the five-coordinated structure containing the five-membered ring structure as shown.



(III)

Each 1,2-bis(ethoxycarbonyl)ethyl group in (II) has an asymmetric carbon atom. In the low-m.p. isomer⁵ of (II), one of the two asymmetric carbons is in the *d*-form and the other, in the *l*-form. In the high-m.p. isomer⁶, however, both of them are in either the *d*-form or the *l*-form. (III) might be a mixture of stereoisomers since it was synthesized using a mixture of stereoisomers of (II) described above and showed a 2° melting range even after repeated recrystallization.

EXPERIMENTAL

General

Molecular weight determinations were performed using a Mechrolab vapor pressure osmometer in chloroform solution. IR spectra were run in KBr pellets or benzene solution using a Hitachi EPI-2G grating spectrophotometer, NMR spectra in chloroform-*d* solutions at 60 MHz using a Japan Electron Optical Laboratory Co. Ltd. model 3H-60 with tetramethylsilane as an internal standard.

[1,2-Bis(ethoxycarbonyl)ethyl]tin trichloride

In a 300 ml, three-necked flask, fitted with two 100 ml separatory funnels and a reflux condenser topped with a phosphorus pentoxide tube, was added (II) (30 g, 0.048 mole), stannic chloride (30 g, 0.115 mole) and carbon tetrachloride (70 ml) and the mixture was refluxed for 4.5 h. After 1 day, the product was quickly filtered to

give 36 g (94%) of solid, m.p. 106.5–110.5°. After repeated recrystallization from 350 ml portions of cyclohexane, 7.2 g white crystals (m.p. 108.5–110.5°) were obtained. (Found: C, 24.20; H, 3.15; Cl, 27.08; Sn, 29.64; mol.wt., 422. $C_8H_{13}Cl_3O_4Sn$ calcd.: C, 24.13; H, 3.29; Cl, 26.71; Sn, 29.81%; mol.wt., 398.) A fuming liquid also was obtained from the filtrate, 11.5 g, b.p. 60–92°/60 mm. (Found: Sn, 33.86%.)

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